

H₂S REMOVAL FROM FUEL GAS DURING COAL GASIFICATION

by

Javad Abbasian, Amir Rehmat
Institute of Gas Technology, 3424 S. State Street, Chicago, IL 60616

Dennis Leppin
Gas Research Institute, Chicago, IL

Daniel D. Banerjee
Center For Research on Sulfur in Coal, Carterville, IL

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Introduction

The United States has large reserves of high-sulfur, caking Eastern bituminous coal. Because of the restrictive environmental emission requirement, this coal cannot be used directly for generation of power, unless the station is equipped with sulfur dioxide scrubbers, which raises the cost of power. One approach to meet the environmental emission requirement and to maintain or improve the overall power generation efficiency is the development of hot gas cleanup systems to remove sulfur and particulate contaminants from the fuel gas thereby eliminating the efficiency losses associated with the cold gas cleanup methods such as wet scrubbing.

Simplicity, efficiency, and cost containment are all integral parts of the development of the sulfur removal systems. An attractive system for coal gasification is one in which high-sulfur coal is gasified; sulfur in the coal is retained within the gasifier with ash, eliminating the need for gas cleanup; gas is available for use without first cooling it to preserve the sensible energy; and water vapor is retained in the product gas to make a substantial contribution in the combined-cycle power output. These criteria can be met through the use of a calcium-based sorbent such as limestone or dolomite directly in the fluidized-bed gasifier, which acts as both a catalyst for the gasification reactions and captures sulfur as calcium sulfate.

The Institute of Gas Technology (IGT) has already developed the U-GAS Process to produce fuel gas from coal. The U-GAS process uses a single-stage fluidized-bed reactor to efficiently convert any type of coal, either run-of-mine or washed, into low- or medium-Btu fuel gas that can be used in industrial plants or utility power plants.(2) The process has been developed during 10 years of testing in a 30 tons of coal per day capacity pilot plant located in Chicago and is currently being commercialized. In a new configuration of the U-GAS process, the U-GAS One-Step Desulfurization Process, limestone or dolomite is fed into the coal gasifier to capture and remove sulfur compounds from the fuel gas within the gasifier. Under the reducing conditions of the gasifier, limestone reacts with sulfur compounds to significantly reduce the sulfur content of the fuel gas.

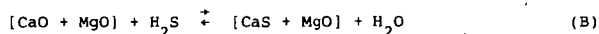
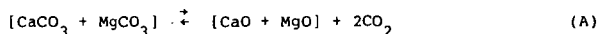
The Gas Research Institute (GRI) was interested in developing a process whereby in-situ desulfurization was used in a coal gasification process to produce power or synthesis gas (for the production of methane) as co-product.(1) Under the sponsorship of GRI and the Department of Energy, a limited number of tests were conducted at pilot plant facilities that verified the feasibility of in-situ sulfur removing techniques(2,3). IGT has recently conducted a series of in-situ desulfurization tests with coal and limestone co-feeding to a high-pressure coal gasifier (see Figure 1). The purpose of these tests was to determine the effects of pressure and temperature on the extent of in-situ sulfur removal within the gasifier. These tests were conducted at gasification pressures ranging from 1 to 3 MPa in the high-pressure Process Development Unit (PDU), which is based on IGT's U-GAS fluidized-bed coal gasification process. The result of these recent high-pressure tests indicates that the approach to equilibrium usually exceeds 84%.(4)

Researchers in the field of chemical kinetics of limestone/dolomite reactions with hydrogen sulfide(5-14) have already verified the potential use of these sorbents for sulfur capture. The reaction of calcined limestone/dolomite is very rapid, and the reaction almost approaches equilibrium. On that basis, it is possible to capture substantial quantities of sulfur and discharge it with the ash. Based on equilibrium considerations, it is feasible to remove up to 90% sulfur using this process.

Work on the desulfurization reactions in the literature has not sufficiently addressed the reaction conditions in the context of coal gasification processes and the kinetics of the sulfidation reaction at the gasification conditions.

This study, which was jointly funded by the Gas Research Institute and the State of Illinois Center for Research on Sulfur in Coal (CRSC), was undertaken to obtain comprehensive experimental data on the sulfidation reactions at gasification conditions to determine the kinetics of this gas/solid reaction.

In the process, the primary sulfidation reactions take place within the fluidized-bed gasifier under reducing conditions. The limestone is calcined at gasification conditions; sulfur capture occurs through the reaction of calcium oxide with hydrogen sulfide:



The specific information obtained in this investigation includes --

1. Determination of the effects of the following variables on the rate of Reaction B.

- Temperature
- Pressure
- H₂S Concentration
- Sorbent Particle Size

2. Determination of the kinetic rate expression for Reaction B as a function of the above variables.

Experimental

The sulfidation reaction tests involving the reaction between CaO and H₂S were conducted in a quartz thermobalance at atmospheric pressure. The effects of sample weight, gas flow rate, particle diameter, H₂S concentration, and temperature on the reaction rate were determined. The thermobalance apparatus and the test operating procedure have been discussed elsewhere(14).

The sorbent chosen for the complete kinetic study in this program was obtained from New Enterprise Stone & Lime Co., Inc., located in Pennsylvania. This material has already been used by the Institute of Gas Technology (IGT) and KRW Energy Systems, Inc. in fluidized-bed gasification tests. Elemental analysis were conducted on this sorbent, the results of which are given in Table 1.

The sorbent (dolomite) was screened and divided into four batches of different particle size range. The range of particle size for the four batches was -80, -45+50, -25+30, and +16 mesh. The complete particle size distribution is given in Table 2.

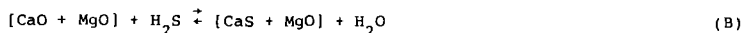
Previous investigation(15) had indicated that the reaction of CaO with H₂S does not depend on the gas composition as long as a constant level of H₂S is maintained. Therefore, in all the tests conducted in this study, the reactant gas consisted of H₂S/H₂/He mixtures. The ratio of hydrogen to hydrogen sulfide was maintained at about 3:1 to prevent dissociation of hydrogen sulfide to elemental sulfur.

To determine the effect of hydrogen sulfide on the reaction rate, and the order of the reaction with respect to H₂S concentration, a series of four tests were conducted with a sample from batch No. 1 (-80 mesh) at 980°C. The concentration of H₂S in this series of runs was 0.8%, 1.6%, 2.5%, and 3.75%. A plot of CaO conversion versus time is presented in Figure 2.

Sulfidation reaction tests were conducted using samples from batch nos. 1, 3, and 4 to determine the effect of intraparticle diffusion on the reaction rate. These tests were conducted at 980°C with a reactant gas containing 3.75% hydrogen sulfide. Figure 3 shows the conversion of calcium oxide versus time as a function of particle size.

Results and Discussions

The conversion of calcium oxide in the sulfidation reaction is calculated using the following formula:



$$\% \text{ Conversion} = \frac{56 \times (\text{weight gained})}{16 \times (\text{calcined sample weight}) \times (\% \text{ CaO in the calcined sample})} \quad (1)$$

where 16 is the difference in the atomic weight of gained sulfur and lost oxygen and 56 is the molecular weight of calcium oxide.

The rate expression for Reaction B is --

$$-r_{\text{CaO}} = \frac{-1}{S_r} \frac{dN_{\text{CaO}}}{dt} = \bar{K}_s [\text{H}_2\text{S}]^n \quad (2)$$

where r_{CaO} is the rate of the reaction, N_{CaO} is the number of moles of calcium oxide, S_r is the surface of unreacted core of the particle, $[\text{H}_2\text{S}]$ is the concentration of hydrogen sulfide, and \bar{K}_s is the overall reaction rate constant.

Assuming the particles are spherical, Equation 2 can be written as --

$$-r_{\text{CaO}} = \frac{-1}{4\pi r_c^2} \frac{dN_{\text{CaO}}}{dt} = \bar{K}_s [\text{H}_2\text{S}]^n \quad (3)$$

The rate constant \bar{K}_s can be expressed as --

$$\bar{K}_s = \frac{1}{\frac{1}{K_d} + \frac{1}{K_s}} \quad (4)$$

K_s is the intrinsic reaction rate constant and K_d is the measure of the conductance due to diffusion. The intrinsic reaction rate constant is usually expressed in Arrhenius form --

$$K_s = K_s^0 \text{Exp}(-E_a/R_g T) \quad (5)$$

where E_a is the activation energy for the reaction, T is the absolute temperature, and R_g is the ideal gas law constant. The diffusion conductance is usually expressed as --

$$K_d = \frac{D_{\text{eff}}}{L} \quad (6)$$

In Equation 6, D_{eff} represents the effective diffusivity and L is the average thickness of the diffusion layer.

Integrating Equation 3, it can be shown that --

$$1 - (1 - x_{\text{CaO}})^{1/3} = \frac{t}{\tau} \quad (7)$$

where

$$\tau = \frac{\rho_{\text{CaO}} R}{K_s [\text{H}_2\text{S}]^n} \quad (8)$$

In the above equations τ is the time required for complete reaction of a particle, x_{CaO} is the conversion of calcium oxide, ρ_{CaO} is the molar density of the sorbent, R is the average radius of the solid particles, and t is the time of reaction. It follows that $1 - (1 - x_{\text{CaO}})^{1/3}$ should be a linear function of time and the slope of such linear plot will be $1/\tau$. A plot of $1 - (1 - x_{\text{CaO}})^{1/3}$ versus time is presented in Figure 4. The order of reaction with respect to hydrogen sulfide concentration was obtained by determining the slope of the line when $\ln(\tau)$ was plotted against $\ln([\text{H}_2\text{S}])$ (Figure 5), indicating that the reaction is first order with respect to hydrogen sulfide concentration (that is, $n=1$).

From the experimental data of this study, the value of intrinsic rate constant was obtained to be 2.99 cm/s, while the effective diffusivity within the solid particle was determined to be 0.692 cm²/s. The diffusivity of hydrogen sulfide in a binary mixture of H₂S/He was calculated using the correlation by Fuller, *et al*(16) to be 7.97 cm²/s. The ratio of the effective diffusivity of H₂S within the solid particle to the open space diffusivity is 0.086. This ratio was reported by Pell(8) to be 0.056.

Tests for the effect of temperature on the sulfidation reaction rate were conducted in the temperature range of 650° to 1040°C. Figure 6 shows the Arrhenius plot of the intrinsic rate constant versus reciprocal of absolute temperature. The slope of this curve indicates that the activation energy for this material in the temperature range of 650° to 1040°C is about 7.7 Kcal/g mole. The overall rate of reaction can be written as --

$$\frac{-1}{4\pi r_c^2} \frac{dN_{\text{CaO}}}{dt} = \frac{-1}{4\pi r_c^2} \frac{dN_{\text{H}_2\text{S}}}{dt} = \left(\frac{1}{\frac{R}{2D_e} + \frac{1}{66.44} \exp\left[\frac{3889}{T}\right]} \right) [\text{H}_2\text{S}] \quad (9)$$

In Equation 9, R is the average diameter of sorbent particles in cm, T is the reaction temperature in °K, and $[\text{H}_2\text{S}]$ is the concentration of hydrogen sulfide in gram mol/cm³.

Integrating Equation 10 leads to --

$$1 - (1 - x_{\text{CaO}})^{1/3} = \left(\frac{1}{\frac{R}{2D_e} + \frac{1}{66.44} \exp\left[\frac{3889}{T}\right]} \right) \frac{[\text{H}_2\text{S}]}{\rho_{\text{CaO}} \cdot R} \cdot t \quad (10)$$

where ρ_{CaO} is the molar density of CaO in gram mol/cm³ and X_{CaO} is extent of conversion of calcium oxide.

The intraparticle diffusivity was calculated by applying the correlation by Fuller, et al(16) to the experimental data from this work. The resulting correlation is —

$$D_e = 2.6 \times 10^{-6} T^{1.75} P^{-1} \quad (11)$$

where D_e is in cm²/s, T is in degrees Kelvin and P is in atmosphere.

The results of experimental tests conducted at elevated pressure (0.2 to 3 MPa) indicated that the overall reaction rate observed in the high pressure thermobalance reactor is controlled by a combination of gas film diffusion and interparticle diffusion. The effective diffusivity and the intrinsic reaction rates could not be determined from the high pressure data.

Conclusion

The rate of reaction between a fully calcined dolomite and hydrogen sulfide have been determined and described by a rate expression that is first order with respect to hydrogen sulfide concentration. The overall reaction rate is controlled by the chemical reaction and intraparticle diffusion. The shrinking core model for spherical particles with unchanging size appears to fit the observed data very well. The activation energy was 7.7 Kcal/g mol and the effective diffusivity through the pore of the solid sorbent at 980°F and 1 atmosphere was 0.692 cm²/s, which is 8.6% of the effective diffusivity of hydrogen sulfide in gas phase.

ACKNOWLEDGEMENT

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Table 1. ELEMENTAL ANALYSIS OF THE SORBENT

<u>Analysis</u>	<u>wt, %</u>
Calcium	28.5
Magnesium	4.79
Silicon	3.11
Potassium	0.46
Iron	0.34
Strontium	0.10
Carbon Dioxide	40.84

Table 2. PARTICLE SIZE DISTRIBUTION OF THE SORBENT USED

<u>Size</u>		<u>Batch No. 1</u>	<u>Batch No. 2</u>	<u>Batch No. 3</u>	<u>Batch No. 4</u>
		<u>(-80 mesh)</u>	<u>(-45+50 mesh)</u>	<u>(-25+30 mesh)</u>	<u>(+16 mesh)</u>
<u>Micron</u>	<u>Sieve (mesh)</u>	<u>wt % retained</u>			
1400	14	--	--	--	--
1180	16	--	--	--	100
710	25	--	--	--	--
600	30	--	--	100	--
355	45	--	0.80	--	--
300	50	--	99.2	--	--
180	80	8.83	--	--	--
150	100	57.10	--	--	--
75	200	10.73	--	--	--
45	325	9.78	--	--	--
	Pan	13.56	--	--	--
		100.00	100.00	100.00	100.00

$$\bar{d}_p = \sum_i \bar{d}_{pi}$$

140 μ 327 μ 655 μ 1290 μ

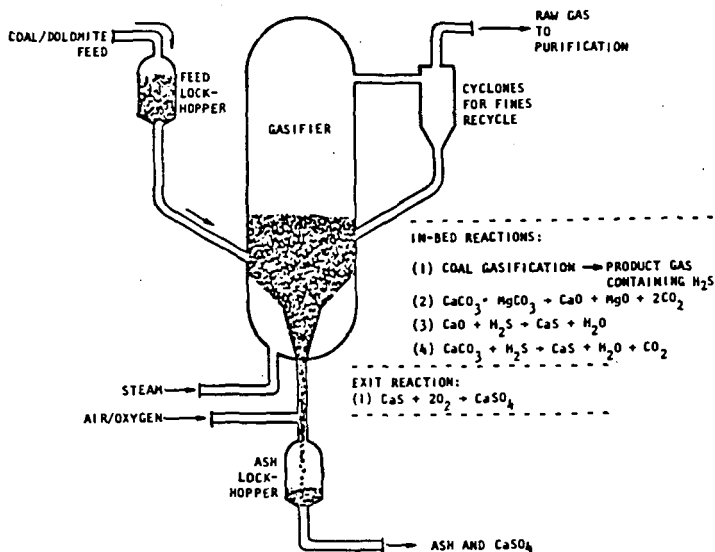


Figure 1. COAL GASIFICATION WITH IN-SITU SULFUR CAPTURE

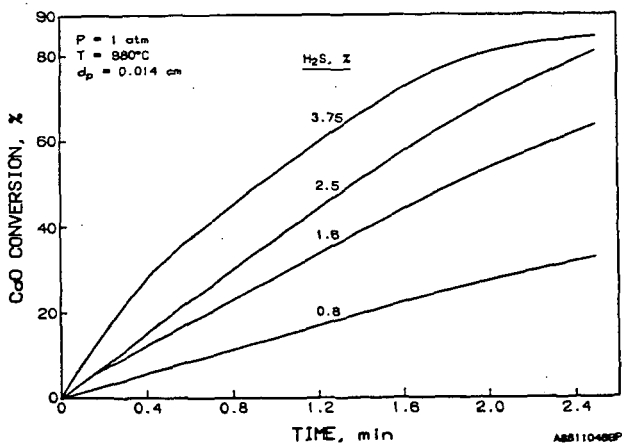


Figure 2. THE EFFECT OF H_2S CONCENTRATION ON THE SULFIDATION REACTION RATE

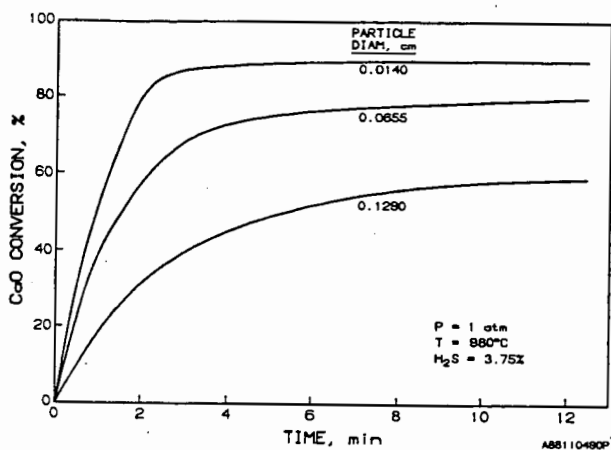


Figure 3. THE EFFECT OF PARTICLE SIZE ON THE SULFIDATION REACTION RATE

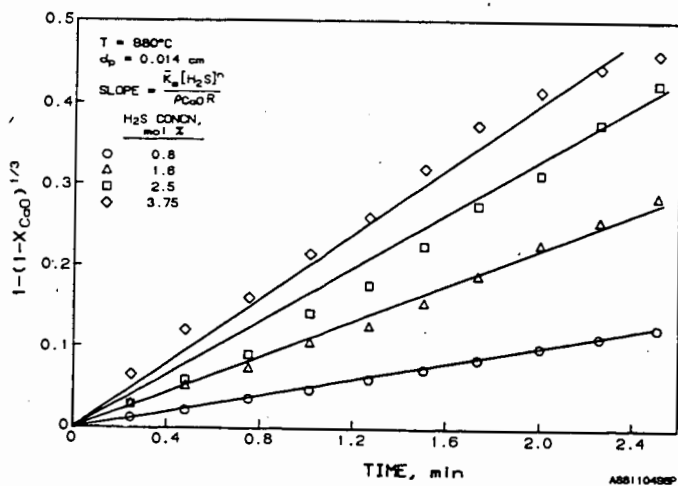


Figure 4. PLOT OF $1-(1-X_{\text{CaO}})^{1/3}$ VERSUS TIME

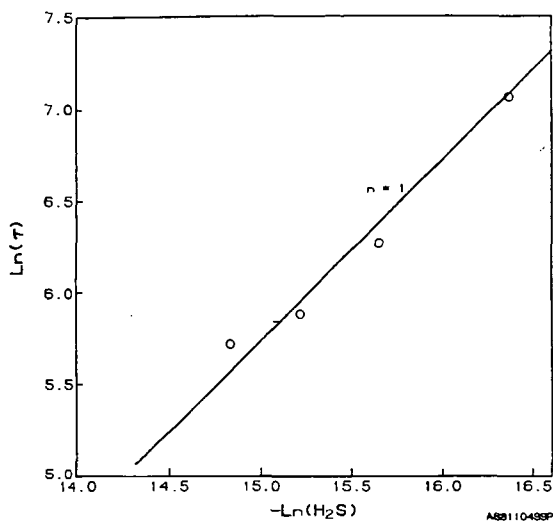


Figure 5. DETERMINATION OF THE ORDER OF THE SULFIDATION REACTION WITH RESPECT TO H_2S CONCENTRATION

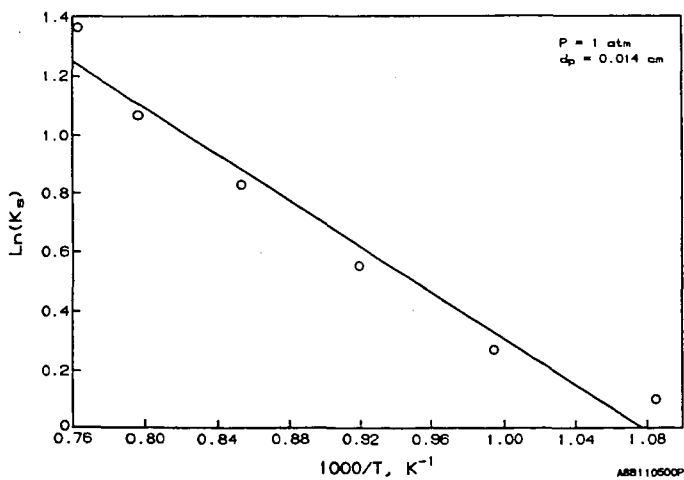


Figure 6. ARRHENIUS PLOT FOR THE SULFIDATION REACTION